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METHOD FOR DISSOLUTION OF
NITROGEN-RICH INCLUSIONS IN TITANIUM
AND TITANIUM ALLOYS

FIELD OF THE INVENTION

5 The present invention relates generally to dissolution of nitrogen-rich inclusions in titanium alloys. More particularly, the invention relates to removal of nitrogen-rich inclusions using electroslag remelting and a halide flux.

10 BACKGROUND OF THE INVENTION

Aircraft jet-engine components operating in the temperature range of about 200 to 500°C are frequently fabricated from titanium-base alloys. Often, the aircraft components are subjected to intense levels of cyclic stress and therefore the dominant mode of mechanical failure is low cycle fatigue (LCF). Such failures start at an initiation site and then grow by crack growth.

15 Initiation of the crack is not an intrinsic property of the titanium alloy. Initiation occurs at an initiation site that is a region that can be chemically or structurally different from the basic titanium alloy. Initiation sites are characterized as hard or brittle precipitates and inclusions, voids, combinations of the two, or other different regions. The larger the initiation site, the longer the initial crack, the faster the initial crack growth rate and the shorter the low cycle fatigue life. Thus there is a need to minimize the size of the initiation site.

25 Initiation sites for low cycle fatigue failure of titanium-base alloy jet-engine components frequently occur at nitrogen-rich inclusions. A nitrogen-rich inclusion is often referred to as a "hard alpha" inclusion in the titanium-base alloy. The core of the inclusion is titanium nitride (TiN) which is surrounded by a layer of a-titanium, which in turn is surrounded by a layer of b-titanium. In some cases the core of TiN might be absent and the a-titanium region might be more extensive.

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"Hard alpha" inclusions (nitrogen-rich) are very brittle when compared to the surrounding titanium-base alloy. As a result, the areas with nitrogen-rich inclusions are the first to crack under intense cyclic stress, thus forming an initiation site. To exacerbate the situation further, the presence of the "hard alpha" inclusion frequently causes a void to form during forging or hot forming, thus increasing the size of the potential initiation site still further.

The overall process for titanium-base alloys, starting with the ore and ending with the component assembled into an engine, takes many steps. The first step is the enrichment of the titanium dioxide from ores, followed by production of titanium tetrachloride, the reduction of titanium tetrachloride to titanium sponge, the preparation of the primary titanium-base alloy electrode, followed by multiple arc meltings or arc plus hearth melting, and last thermomechanical processing of the ingot.

The nitrogen-rich inclusions of concern in the titanium-base alloys are created as defects during the refining steps of the process and are not successfully dissolved during the melting steps, such as the preparation of the primary electrode, the multiple arc meltings or arc plus hearth melting, and the thermomechanical processing of the ingot. Chopping the refined titanium into smaller pieces and using melting schemes with longer melt residence times, such as triple arc melt and hearth melt, have helped, but can not guarantee elimination of inclusions. Currently, ultrasonic inspection is being used at several stages along the processing route after melting to find and discard materials containing nitrogen-rich inclusions. This is time consuming and expensive.

For the above reasons, there is an increased need to eliminate or minimize the size of nitrogen-rich inclusions in titanium and titanium-base alloys.

SUMMARY OF THE INVENTION

This invention is directed toward a process for the electroslog remelting of titanium and titanium alloys which will ensure

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that nitrogen-rich inclusions are dissolved or at least minimized during the melting process. The approach is a derivative of electrosag remelting (ESR) applied to titanium-base alloys.

Briefly, electrosag remelting can be described as a process where the material to be refined, the electrode, is melted by passing a current through it into a molten flux or slag, which is resistively heated and which, in turn, melts the electrode. Molten metal forms on the end of the electrode and falls as droplets through the flux, forming an ingot in a cooled crucible. The process continues until the electrode is consumed and the refined metal ingot is formed.

In this invention, the halide flux, also referred to as slag, is primarily a calcium halide, such as calcium fluoride (CaF_2) or calcium chloride. Calcium fluoride is preferred. The halide flux, such as calcium fluoride, has suitable additions, such as dissolved metals and oxides. Calcium metal is a preferred addition and is sufficient in the slag in a sufficient amount to aid in lowering the partial pressure of nitrogen and oxygen in the flux, while increasing the conduction of the flux.

The term "nitrogen-rich inclusion" means a titanium nitride (TiN) core surrounded successively by a layer of alpha-titanium (α -Ti) and a layer of beta-titanium (β -Ti), with decreasing nitrogen concentration and decreasing chemical activity of nitrogen from the center of the inclusion to its outer surface. The nitrogen-rich inclusion is surrounded by the β -Ti electrode, which typically has a nitrogen content of approximately 50 wppm.

Dissolution of the nitrogen-rich inclusion takes place by transport of titanium and nitrogen from the electrode into the flux as the flux flows past the exposed surface of the titanium nitride inclusion. The exposed surface of the titanium inclusion is located on the face of the electrode that is in contact with the molten flux. The nitrogen is transported to the liquid metal film on the face of the electrode, where it is re-absorbed. Because nitrogen is continually re-absorbed by the liquid metal film, the chemical activity of nitrogen (represented by its partial pressure) in the flux is maintained lower than that in the

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inclusion, but higher than that at the liquid metal film/flux interface. As a result, thermodynamic driving forces in the liquid metal film and in the flux always exist to transport nitrogen away from the inclusion. The nitrogen partial pressures in equilibrium with different regions of the nitrogen-rich inclusion and the liquid metal film on the electrode face can be calculated.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic view of the electroslag refining of a titanium alloy electrode showing the nitrogen-rich inclusion at the electrode/flux interface.

FIG. 2 is a schematic view of dissolution of the nitrogen-rich inclusion in the flux based on the partial pressures of nitrogen.

DETAILED DESCRIPTION OF THE INVENTION

It has been discovered that electroslag remelting of titanium metal or alloys under controlled partial pressures of nitrogen, and somewhat oxygen, can dissolve nitrogen-rich inclusions to help eliminate or reduce initiation sites for cracks.

One aspect of the invention is a method of removing nitrogen rich-inclusions from a titanium containing electrode, comprising the steps of: contacting a bottom surface of the titanium containing electrode with a flux in a crucible; passing a sufficient amount of electric current through the electrode and flux to melt the bottom surface of the electrode while resistively heating the flux at a temperature that melts the bottom of the electrode; and dissolving the nitrogen-rich inclusions exposed to the flux by maintaining a nitrogen partial pressure in the flux lower than that in the inclusion.

Another aspect of the invention is the article made by the above method.

Still another aspect of the invention is a method to refine titanium or titanium alloys by electroslag refining, comprising the steps of: heating in a non-oxidizing atmosphere a calcium halide flux containing about 1 - 4.5 weight percent calcium metal to a temperature above about 1600 C; stirring the flux with a magnetic or arc stirring

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means; touching the flux with a titanium or titanium alloy electrode containing nitrogen-rich inclusions; applying an alternating current to the titanium or titanium alloy electrode, which passes through the flux to resistively heat the flux; and maintaining a partial pressure of nitrogen in the flux below the partial pressure of nitrogen in the inclusion.

The calcium metal in the flux helps to provide low partial pressures of nitrogen and oxygen while increasing the conduction of the flux. A preferred range for the partial pressure of nitrogen in the flux is about 10^{-12} to 10^{-15} atmospheres and for oxygen about 10^{-20} to 10^{-25} atmospheres. Decreasing the flux resistance aids the elevation of the temperature of the flux, which in turn provides the appearance of the generation of microarcs on the surface between the flux and the end of the consumable electrode. Nonmetallic inclusions are crushed by these microarcs, partially or fully.

The low partial pressure of nitrogen changes the stoichiometry of titanium nitrides. For example, titanium nitride, TiN, may be transferred to $\text{TiN}_{0.98}$ or $\text{TiN}_{0.95}$. The low partial pressure of oxygen increases the sorption characteristics of the nitrogen in the flux.

Illustrated schematically in Figure 1 is a view of the electroslag remelting system depicting titanium or titanium alloys with a nitrogen-rich inclusion. The system 10 includes a titanium or titanium alloy electrode 12 with a nitrogen-rich inclusion 14 at the interface 16 between the electrode 12 and the halide flux 18. The electrode 12 forms molten metal droplets that fall through the flux 18 and are collected as liquid metal 20. The system includes a crucible 22 in which is suspended the electrode 12, the flux 18, and liquid metal 20. Conventional means are provided for melting the bottom end 24 of the electrode 12 as it is fed into the crucible 22. The heating means include a suitable alternating current power supply electrically joined to the electrode. Electrical current is carried through the electrode 12 and through the flux 18, in liquid form, to the crucible

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22. In this way, the flux 18 is resistively heated to a suitably high temperature to melt the bottom end 24 of the electrode.

The electrode 12 or otherwise known as the ingot to be refined or remelted, is formed of titanium or any suitable titanium alloy requiring electroslog remelting. Examples of titanium alloys are Ti-6Al-4V, Ti-6Al-2Sn-4Zr-2Mo, and Ti-17-(5Al-4Mo-4Cr-2-Sn-2Zr). A suitable flux 18 is a halide flux, in particular calcium fluoride. The flux may have additional suitable additions, such as dissolved metals and oxides, including calcium metal in a preferred amount of about 1 to 4.5 weight percent.

Now referring to Figure 2, the nitrogen-rich inclusion 14 is composed of an inner core of titanium nitride (TiN) 26, followed by alpha-titanium section 28, and an outer section called beta-titanium 30. The nitrogen-rich inclusion 14 can be up to about 1200 micrometers in diameter, and often is in the range of about 300 to 1000 micrometers in diameter. The end 24 of the electrode 12 is a liquid titanium film about 30 to 100 micrometers thick. The titanium electrode 12 generally contains up to about 50 weight parts per million (wppm) nitrogen. This is not the nitrogen-rich inclusion 14.

As the nitrogen-rich inclusion 14 moves through the liquid film 24 on the electrode 12, the beta -titanium 30 on its front face equilibrates with the liquid film 24. For instance, if the superheat in the liquid film 24 is 10 °C, the beta-titanium 30 at the inclusion/flux interface 32 has an effective nitrogen partial pressure corresponding to saturated liquid in equilibrium with beta-titanium at that temperature. The rest of the liquid film 24 is undersaturated at 50 wppm nitrogen and corresponds to a lower nitrogen partial pressure. The decomposition nitrogen partial pressure for stoichiometric titanium nitride (TiN) is approximately 10^{-10} atmospheres. The driving force for nitrogen transfer from the inclusion into the flux is the two orders of magnitude difference between the nitrogen partial pressure at the inclusion/flux interface 32 and the nitrogen partial pressure at the liquid metal film/flux interface 16. The nitrogen partial pressure in the flux 18 must fall between these two values. If the driving force shown

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is not adequate, the inclusion will protrude from the liquid metal surface, and its temperature will increase. The nitrogen partial pressure corresponding to liquid/beta-titanium equilibrium will increase with increasing temperature until a sufficient driving force is available to remove nitrogen from the inclusion at an adequate rate. As the lower-nitrogen outer regions of the inclusion are removed, the nitrogen chemical activity or partial pressure in the exposed inclusion increases, thus the nitrogen removal rate should increase as the inclusion continues to dissolve.

It has further been discovered that several factors must exist for the nitrogen transport process to be effective. First, an adequate thermodynamic driving force must exist near the beginning of the process, when the concentration difference between the outer layer of the inclusion and the liquid metal film on the electrode is small. Second, the chemical activity of nitrogen in the flux must fall between that at the inclusion/flux and liquid metal film/flux interfaces. Third, the nitrogen solubility in the flux and the flux velocity must be adequate so that the flux does not come into thermodynamic equilibrium locally with the inclusion, and so that nitrogen is transported at an adequate rate from the inclusions to the liquid metal film on the electrode. Fourth, the nitrogen removal rate from the flux into the liquid metal film by interfacial transfer and diffusion in the liquid metal must be high enough to keep the process going. Fifth, the nitrogen capacity of the liquid metal layer must be high enough to absorb all of the nitrogen transported from the inclusions.

The nitrogen may go into solution as an ion, as a neutral dissolved species, or as a complex ion with oxygen or some other species. Rapid circulation of the flux to move nitrogen away from the inclusion is suggested. The flow rate of the flux past the inclusion is important and can be augmented independently of temperature by arc and magnetic stirring.

It is essential that the various kinetic processes listed above are fast enough so that the nitrogen-rich inclusion dissolves at a rate at least as fast as the melting back of the electrode face. Since

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the chemical activity of nitrogen in the flux is low, it is also essential that additional nitrogen is not introduced into the flux from the surrounding atmosphere. An inert gas, which may have to be gettered to produce the required low nitrogen partial pressure, must be maintained above the exposed flux. Generally, the electrode melting is done in a non-oxidizing environment, such as argon, helium, neon, hydrogen or mixtures thereof.

Additions to the calcium halide-based flux which would aid in nitrogen dissolution may also be beneficial. Oxygen in the form of a dissolved oxide such as calcium oxide (CaO) or titanium oxide (TiO), might be used to oxygenate the center of the inclusion, reducing its melting temperature and enhancing diffusion and dissolution. Solubility of calcium and oxygen in calcium-rich calcium halide, such as calcium chloride (CaCl₂) fluxes has been demonstrated.

Thermodynamic calculations have been used to indicate that dissolution of a nitrogen rich-inclusion is possible by electroslag refining (ESR). The results of these calculations are shown schematically in Figure 2. The titanium nitride core of the inclusion is surrounded successively by a layer of alpha-titanium and a layer of beta-titanium, each layer with a decreasing nitrogen concentration and decreasing chemical activity of nitrogen. The inclusion is shown embedded in a beta-titanium electrode, which typically has a nitrogen content of approximately 50 parts per million by weight (wppm). It is demonstrated that dissolution of the inclusion will take place by transport of nitrogen into the flux, as the flux flows past the exposed surface of the inclusion. The nitrogen will then be transported to the liquid metal film on the face of the electrode, where it will be re-absorbed in a widely dispersed fashion. This layer will melt, and droplets will pass through the flux to form a solidified ingot below. For this approach, the electroslag refining system must be capable of maintaining a partial pressure of nitrogen in the flux and in the atmosphere above the flux of less than 10^{-15} atmospheres.

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Examples:

Example 1. The interaction of titanium nitride (TiN) with a calcium fluoride-base flux has been observed in the laboratory, by immersion of a sample of hot isostatic pressed titanium nitride (TiN) in a 70% calcium fluoride (CaF₂), 15% calcium oxide (CaO), 15% aluminum oxide (Al₂O₃) flux. The flux was heated in a graphite crucible by induction heating. Breakup of the titanium nitride (TiN) was noted.

Example 2: Inclusion Preparation - Two types of inclusions were prepared by GE-CRD. Inclusions with Identification Number 30 were fabricated by placing nitrated sponge and titanium powder in titanium alloy tubes. The tubes were sealed with plugs by electron beam welding. The tubes were then isostatically pressed at 1200°C / 1000 atm. / 4 hr. Samples were cut from these tubes with 12.5 mm diameter by 10 mm length. The nitrogen containing portion of each sample was 10 mm diameter.

Inclusions with Identification Number 49 were fabricated by placing titanium nitride powder in titanium alloy tubes. The tubes were sealed with plugs by electron beam welding. The tubes were then isostatically pressed at 1200°C / 1000 atm. / 4 hr. Samples were cut from these tubes with 12.5 mm diameter by 10 mm length. The nitrogen containing portion of each sample was 10 mm diameter.

Inclusion information is summarized in Section 1 of the attached table 1.

Electrodes were prepared by pressing titanium sponge into cylinders 60 mm in diameter by approximately 250 to 275 mm long. Two such cylinders (plus a top attachment stub) were welded together by TIG welding to form an electrode. Holes (13 mm diameter) were drilled into the sides of the electrodes to a depth of approximately 13 mm. Inclusions were inserted into these holes and welded into place by TIG welding. The inclusion types and positions (measured from the bottom of the electrodes) are summarized in Section 2 of the attached table 1.

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The electroslag refining system used for these examples was of the type having a water cooled crucible, approximately 95 mm inside diameter by 360 mm long and capable of producing an ingot up to 200 mm in length. The electrode was placed inside a water cooled chamber mounted above the water cooled crucible. The crucible and chamber were evacuated and then back filled with argon before melting. The system was kept at a positive pressure of argon of 0.15 atmospheres during melting. A small flow of argon occurred to compensate for leakage out the various seals in the system. The flux used for these experiments was made up from 1000 grams of calcium fluoride and 20 grams of metallic calcium. Calcium vapor rises into the chamber above the crucible and reacts with the small amounts of nitrogen (and oxygen) in the argon to reduce the partial pressure of nitrogen in the atmosphere above the flux to less than the required 10^{-15} atmospheres.

A typical melting run consisted of a starting period (at low current) to melt the flux, followed by a melting period (at higher currents) to melt the electrode. Melting was carried out at the melting currents summarized in Section 3 of the attached table 1. A time of about 7 to 10 minutes was required for the completion of melting. An average grain size of about 2 to 4 mm was observed on the top surface of these ingots. The refined ingots are the metal that has been collected after electroslag remelting of the electrode.

The ingots were machined on the circumference and the top and bottom surfaces to prepare them for ultrasonic inspection. A Model 11YA Ultrasonic Defect Tester was used. This instrument was capable of frequencies of 1.25, 2.5, 5 and 10 MHz. A frequency of 2.5 MHz was selected for this examination. Inspection was conducted with the transducer placed on either the top or the bottom surface of the ingot. A drop of glycerin was placed between the transducer and the ingot surface to provide good contact. In order to adjust the instrument, a calibration block was prepared from a pure titanium ingot, with 1.5 and 2.5 mm diameter holes drilled into the side at three locations along the length of the ingot. The instrument was calibrated

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to give approximately the same amplitude of indication from each of the three holes, whether viewed from the top or viewed from the bottom of the ingot. These adjustments then remained unchanged during measurement of the five ingots prepared from electrodes containing inclusions.

All ingots showed some small indications in the top 20 mm of length, particularly at the centerline. It was assumed that these indications were from shrinkage porosity formed by rapid solidification at the top of the ingot, when the melting current was turned off.

At least one major ultrasonic indication was observed in each ingot. The number of indications and positions (measured from the bottom of the ingots) are summarized in Section 3 of the attached table 1. All indications, except for one, occurred at positions in the lower 15 to 30% of the length of the ingot. Their position can not be correlated with the positions of the inclusions in the electrodes. It is assumed that they represent disturbances caused when the melting current was changed from the low current of the starting period (flux melting) to the high current of the melting period (electrode melting). In ingot D6, one large indication occurred (at 58 mm from the bottom) near the location of the lower inclusion in the electrode that was melted. This particular inclusion was only welded to the electrode in two places and may well have fallen into the liquid metal pool during melting.

The results from the preliminary ultrasonic inspection showed that there are no large inclusions in the ingots.

TABLE 1.

1. Inclusions

Identification Number	Color	Type	Isostatic Press	% N
30	Silver	Ti Sponge	1200°C/1000 Atm./4Hr.	15
49	Yellow	TiN Powder	1200°C/1000 Atm./4Hr.	22

2. Electrodes

Electrode Number	Diameter mm	Length mm	Inclusion Type	Position mm	Weld	Position mm
N3	60	515	49	300	1	255
N4	60	550	30, 30	170, 335	1	255
N5	60	535	30, 49	205, 355	1	215
N6	60	530	49, 30	210, 355	1	215
N7	60	480	30, 49	260, 385	4	85, 175, 330, 430

3. Ingots

Ingot Number	Diameter mm	Length mm	Electrode Number	Melting Current kA	Ultrasonic Indications	Position
2	88	137	N3	4	1	48
3	89	121	N4	5-7	1	38
4	86	130	N5	3-4	1	38
5	88	122	N6	3-4	3	19, 25, 31
6	87	112	N7	3-4	4	17, 22, 32, 58